

# PATENT SPECIFICATION

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## (54) METHOD FOR PREVENTING THE LOSS OF REACTANTS IN THE PRESSURIZED SYNTHESIS LOOP

(71) We, TOYO ENGINEERING CORPORATION, a Japanese Corporation, of No. 5, 3-chome, Nihonbashi-Honcho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for preventing the loss of reactants when exhausting residual gas during the synthesis of ammonia or methanol.

In the synthesis of ammonia or methanol, unreacted materials are commonly recirculated through a reaction zone. Such systems are commonly referred to as "circulatory synthesis systems". In circulatory synthesis systems, inert gases, i.e. gases which are not involved in the synthesis reaction, are continuously removed from the circulating stream but this inevitably also involves the removal and loss of some of the reactant gases. Various methods have been proposed to reduce wastage of reactant gases but these methods have all suffered from certain disadvantages, particularly with regard to the capital cost of equipment and the cost of operating it.

This invention relates to the synthesis of ammonia and of methanol, the former being usually operated at a pressure of 150-1000 atm. involving methane and argon as the principal inert gases, whereas the latter operated usually at 300 atm. involving methane and nitrogen as inert gases.

The following explanation, which is chiefly given on the examples of application of such syntheses of ammonia or methanol, does not restrict the general applicability of the invention.

It is well known that ammonia can be synthesized from nitrogen and hydrogen in the presence of a suitable catalyst and under appropriate pressure and temperature conditions, e.g. 150-1000 atm. and 350-550°C.

The synthesis gas, composed of a mixture of hydrogen and nitrogen, is usually prepared by catalytic or non-catalytic cracking of solid

carbon-containing substances or fluid hydrocarbons with steam, air or oxygen, or a mixture thereof in arbitrary ratio under elevated temperature and normal or elevated pressure.

The gas thus obtained from the cracking apparatus is composed of hydrogen, carbon monoxide and carbon dioxide, and usually contains small amounts of nitrogen and argon as well as methane formed by incompleteness of the cracking.

Therefore, the treatments on said crude synthesis gas for obtaining hydrogen or hydrogen and nitrogen necessary for the synthesis of ammonia in a state as pure as possible usually comprise primarily the conversion of carbon monoxide into carbon dioxide and secondarily the removal of carbon dioxide.

After these treatments, the synthesis gas contains methane, argon and small amounts of remaining carbon monoxide and carbon dioxide in addition to hydrogen and nitrogen. Said small amount of remaining carbon monoxide can be eliminated by scrubbing with liquid nitrogen, scrubbing with cuprous salt solution, or methanation. The synthesis gas purified with methods other than scrubbing with liquid nitrogen contains methane and argon in addition to the hydrogen and nitrogen which are necessary for the synthesis of ammonia.

This gas, when compressed and introduced into the ammonia synthesis loop, usually shows relatively low conversion rate to ammonia. The concentration of ammonia at the outlet of a synthesis reactor is usually 10 to 30 per cent by volume for pressures of synthesis of 150 to 1,000 atm.

The synthesis of ammonia can therefore be economically carried out only when the gaseous mixture composed of ammonia, unreacted hydrogen and nitrogen, methane and argon is recirculated to the reactor after ammonia contained therein is separated by condensation or absorption.

It is well known that argon and methane which are not related to the reaction gradually accumulate in the ammonia sy-

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ntesis loop while unreacted hydrogen and nitrogen are converted into ammonia by recirculation, and that these inert gases should therefore be removed from the loop.

5 A well-known proposal for solving this technical subject consists of the continuous removal of a portion of the circulating stream from the loop of ammonia synthesis, thereby maintaining the concentration of inert gases, i.e. methane and argon, in the loop at a constant level. However, it can easily be seen that this method inevitably involves the waste of available hydrogen and nitrogen together with inert gases.

10 The use of a modified copper type shift catalyst for converting carbon monoxide into carbon dioxide, and the use of a methanation process have simplified the removal of carbon monoxide. On the other hand the use of the methanation reaction results in the increase of inert methane and consequently the increase of reactants wasted from the loop of synthesis along with the removed inert gases.

15 According to the invention there is provided a method for preventing the loss of reactants in the pressurized synthesis loop of ammonia or methanol, comprising the steps of separating a portion of the circulating stream of said loop, compressing said portion at least once, causing further synthesis reaction to take place in said portion at least once, recovering the product formed by said reaction, allowing the residual gas to expand, and exhausting the expanding gas; wherein energy derived from expansion of the residual gas is used for the compression of the said portion of the circulating stream.

20 It has been ascertained that an ammonia synthesis apparatus produced ammonia at the rate of 20 kg-mole/hr./m<sup>3</sup>-catalyst at 162 atm. and 400°C. from a mixture containing 10% vol. of inert gases consisting of argon and methane and 9% vol. of ammonia, the balance being a 3 : 1 (by volume) mixture of hydrogen and nitrogen, while the same apparatus with same catalyst produced ammonia at the rate of 30 kg-mole/hr./m<sup>3</sup>-catalyst at 475 atm. and 400°C. from a mixture containing 40% vol. of similar inert gases and 9% vol. of ammonia, the balance being a similar mixture of hydrogen and nitrogen. In other words, a reaction terminated under a certain pressure is again activated and acquires considerable reaction velocity under a higher pressure.

25 Methods according to the present invention can thus be expected to minimize the loss of reactants during the removal of inert gases.

30 Analyses on various synthesis apparatus revealed that an accumulation of inert gases causes a suppression of the synthesis reaction. This is because there is a decrease in the partial pressure of the reactants as a result of an increase in the partial pressure of

the inert gases. Methods according to this invention therefore can also be expected to promote the synthesis reaction, in addition to minimizing loss of reactants.

35 Methods carried out in accordance with the invention can also be expected to consume an exceptionally small amount of power because the energy for compressing the separated portion of the stream is wholly or partly derived from the expansion of residual gas.

40 It is preferable that the energy from the expansion of the residual gas be generated by an expander which is directly mechanically coupled to a compressor for compressing the separated portion of the circulating stream. This can give the advantage that if the energy generated by expansion of the residual gas increases, the pressure of the separated portion of the circulating stream also increases, thereby accelerating the reaction. Acceleration of the reaction causes the volume of the residual gas to decrease and therefore also causes the energy given by the expansion to decrease. Thus the power produced by the expander and consumed by the compressor is automatically balanced.

45 Although the expander and compressor can be of a centrifugal type if the circulating stream to be removed is large, a plunger-type expander and compressor are preferable for apparatus of usual capacity.

50 Hydrogen, when subjected to isentropic expansion at 30°C. from 50 atm. to 20 atm., shows a temperature decrease of about 80°C. and therefore reaches -50°C. Similar effects can be observed in the case of methane and argon. Consequently, if the gas at the inlet of the expander is kept at normal temperature, the gas stream at the outlet, being at fairly low temperature, can be utilised as a refrigerating source.

55 On the other hand, more energy can be recovered if the gas introduced to the inlet of the expander is kept at a higher temperature by means of some heat source of the synthesis apparatus. In this case the refrigeration effect is no longer obtained.

60 In a preferred method according to the invention the ammonia contained in the finally removed stream can be separated by simple water-cooling as the circulating stream to be concentrated is compressed to a high pressure. This contrasts with the more usual separation methods for ammonia, such as the condensation method by deep cooling, or the scrubbing method with water followed by distillation of the resulted aqueous ammonia solution.

65 Since the concentration of ammonia remaining in the gas stream under high pressure can be made very small even by simple water cooling, any ammonia present in the residual gases can be exhausted without appreciable loss. In this preferred

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form of the invention it is therefore scarcely necessary to recover ammonia from the residual gas.

5 An exemplary form of the invention will now be particularly described with reference to the accompanying drawings in which Fig. 1 and Fig. 2 show flow sheets for embodying the method of this invention.

10 In the method of Fig. 1, the synthesis gas contains methane and argon which are inert for the purposes of the synthesis reaction, and hydrogen and nitrogen is introduced, through pipe 1, into the loop for ammonia synthesis composed of heat exchangers 2 and 3, separator 4, circulating compressor 5, heat

15 exchanger 6, reactor 7 and heat exchanger 8. The synthesis gas joins the stream circulating in the loop, then is cooled by the low temperature heat exchanger 2 and further deeply cooled by the heat exchanger 3. Ammonia contained in the circulating stream is condensed and separated, as liquid ammonia, from the pipe 9 of separator 4.

25 The circulating stream from which ammonia is removed is heated in the heat exchanger 2, compressed by the circulating compressor 5, then heated in the heat exchanger 6 by the stream from the reactor 7, and then introduced into the reactor in which hydrogen and nitrogen are converted into ammonia by the presence of catalyst contained in the reactor.

30 The circulating stream containing ammonia and exhausted from the reactor, being at high temperature, are cooled by heat exchanger 8, then further cooled by the heat exchanger 6 and join the newly added synthesis gas.

35 The extraction for removing inert components may be carried out at arbitrary point in this loop. However, in this case, said extraction is done at the point prior to the circulating compressor 5.

40 The stream to be removed is compressed by a compressor 11 which is driven by an expander 10, and introduced into a reactor 12 in which the reaction of ammonia synthesis again takes place.

45 The effluent from the reactor 12 is cooled by a heat exchanger 13. Ammonia present in the effluent is condensed in the heat exchanger and separated, as liquid ammonia, from the pipe 15 of separator 14.

50 These procedures can be repeated, if necessary. Namely the effluent from the reactor 12 is let to pass through a reactor 16, heat exchanger 17 and separator 18, in which liquified ammonia is separated through the pipe 19.

55 The high-pressure residual gas stream from the separator 18, containing inert gases at high concentration, is introduced into the expander 10, in which the gas stream is expanded to generate the power for driving the compressor 11, and exhausted from the

pipe 20 at a pressure close to atmospheric pressure for use as fuel or introduced at an appropriately higher pressure to a deep-cooling separator of well known type (not shown) in which inert gases such as methane and argon are separated. Hydrogen recovered in the deep-cooling separator is mixed to the synthesis gas in the pipe 1.

Fig. 2 shows the process of this invention operated as a circulatory system.

70 The portion of the stream to be concentrated is extracted from synthesis loop at the point in front of the circulating compressor 5, then compressed by the compressor 11 and introduced into a loop consisting of heat exchangers 13, 16 and 17, reactor 12, circulating compressor 21 and separator 14. The stream to be concentrated and the unreacted components compressed so as to compensate the loss of pressure in the loop, are united, preheated by the heat exchanger 13, and introduced into the reactor 12.

75 The effluent from the reactor 12 is cooled by the heat exchangers 16, 13 and 17, and ammonia formed in the reactor and liquified by the heat exchangers is separated in the separator 14 and exhausted from the pipe 15. The gaseous mixture from which liquified ammonia is already separated is compressed by the circulating compressor 21 and united with the stream to be concentrated.

80 A portion of the gaseous mixture from which liquified ammonia is already separated is extracted from this loop at a point between the separator 14 and the circulating compressor 21, and exhausted through the pipe 22, expander 10 and pipe 20 for use as fuel or for use in the deep-cooling separator as explained in the example referring to Fig. 1.

85 The concentration of inert gases in the residual gaseous mixture exhausted from the pipe 20 is much higher than that in the main synthesis loop. The actual advantages of this invention will be explained by an example of ammonia synthesis apparatus capable of producing 660 ton/day of ammonia at 150 atm.

90 The gaseous mixture fed to the ammonia synthesizing loop was composed of 60936 Nm<sup>3</sup>/hr. of hydrogen, 20312 Nm<sup>3</sup>/hr. of nitrogen and inert gases consisting of 658 Nm<sup>3</sup>/hr. of methane and 254 Nm<sup>3</sup>/hr. of argon.

95 Dissolution into the final product, i.e. liquid ammonia, is a possible escaping route of the inert gases from the apparatus. The actual measurement, however, revealed that the amounts escaping from the apparatus by this way only amounted to 96 and 19 Nm<sup>3</sup>/hr. respectively in the case of methane and argon.

100 It was necessary, therefore, to provide another way of removing large amounts of inert gases in order to maintain the

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concentration of these gases in the apparatus at the appropriate level. However, by this way, the loss of hydrogen, nitrogen and ammonia inevitably resulting from the removal amounted to 6143, 2040 and 164 Nm<sup>3</sup>/hr. respectively.

The stream thus removed was compressed to 450 atm., heated by heat exchanger and introduced to a reactor of smaller capacity filled with iron catalyst so as to produce ammonia according to this invention.

Ammonia thus produced was condensed by cooling and separated. The gaseous mixture still containing unreacted reactants after passing through the reactor of smaller capacity was introduced into a similar second reactor of small capacity.

Thus the total concentration of methane and argon in the gaseous mixture after passing through the second reactor and removal of liquified ammonia amounted to 26.6% whereas that at the removal from the main loop was only 9%. In this example the amount of hydrogen recovered as ammonia was 4500 Nm<sup>3</sup>/hr., corresponding to 7.4% of hydrogen fed to the ammonia synthesis apparatus.

Therefore, compared with the case without employing the process of this invention, the power economised amounted to 600 KWH at the high pressure compressor for the synthesis gas, and 400 KWH at the air compressor for supplying compressed air to the second steam reforming furnace for providing nitrogen contained in the synthesis gas.

Furthermore, the power necessary for raising the pressure of the stream to be concentrated from 150 atm. to 450 atm. was almost compensated by the energy obtained by the expansion of gas of 2997 Nm<sup>3</sup>/hr. passed through the second small reactor and second separator from 450 atm. to an atmospheric pressure.

Thus the power totally economised by this ammonia synthesis process reached 1,000 KWH.

In addition to this, the capacities for preparation of synthesis gas, conversion of carbon monoxide, removal of carbon dioxide, removal of carbon monoxide and the high pressure compressor can be made 7.4% smaller. Therefore, the total construction cost can be made about 4% smaller than the construction costs for the equipment for compressing the stream to be concentrated, reactors, heat exchangers and power recovering equipment included.

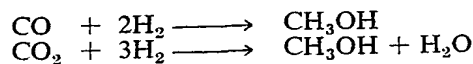
The process of this invention has so far been exclusively explained with regard to the synthesis of ammonia. However, some modifications might become necessary in applying this process to other synthetic processes.

In the case of application to methanol

synthesis, an example of composition (vol. %) of methanol synthesis gas is as follows:

CO	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
18.17	9.41	69.67	1.42	1.33

The amount of hydrogen contained is larger than the stoichiometric amount defined by the following formula:



Usually the amount of hydrogen is represented by the index R calculated by the following formula:

$$R = (\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2)$$

Although the stoichiometric relationship is complete when this index is equal to 2, R is usually chosen as 2.1 or 2.2 in the industrial processes, because the yield of methanol rapidly decreases at R values smaller than 2.

In the case of methanol synthesis with the synthesis gas of the above-described composition (vol. %), the composition of circulating stream to be concentrated is as follows:

CO	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
6.75	3.72	66.78	11.78	10.97

As can be seen from this composition, the R value is excessively large. In applying this invention, it is preferable, therefore, to regulate the value of R by adding carbon monoxide, or carbon dioxide which has larger availability, to the circulating stream to be concentrated. It is also possible to add nitrogen to the stream, after the removal of carbon monoxide and carbon dioxide.

The method of the invention, of concentrating inert gases by the compression of the stream to be removed is not necessarily limited to the use of only one compression. Namely, if the reactants are present in relatively large amount in the stream to be removed, it is possible to repeat the process of compression, synthetic reaction and separation of the desired products thus synthesized.

#### WHAT WE CLAIM IS:—

1. A method for preventing the loss of reactants in the pressurized synthesis loop of ammonia or methanol, comprising the steps of separating a portion of the circulating stream of said loop, compressing said portion at least once, causing further synthesis reaction to take place in said portion at least once, recovering the product formed by said reaction, allowing the residual gas to expand, and exhausting the expanded gas; wherein energy derived from the expansion of the

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residual gas is used for the compression of the said portion of the circulating stream.

2. A method as claimed in Claim 1, wherein before the compressing, necessary reactants are added to said separated portion thereby to regulate the composition of said portion for further synthesis reaction.

5  
10 3. A method substantially as herein described with reference to Fig. 1 of the accompanying drawings.

4. A method substantially as herein described with reference to Fig. 2 of the accompanying drawings.

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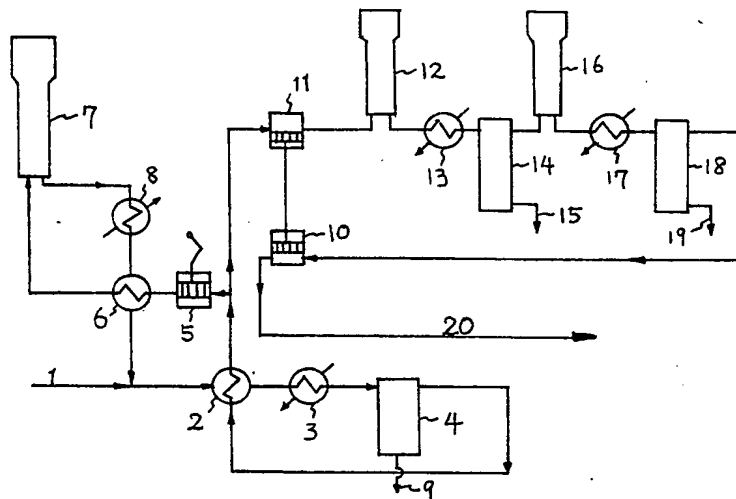
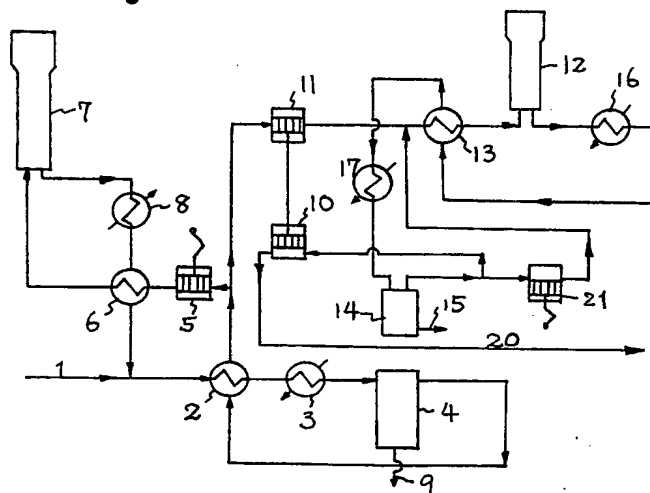
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## COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of  
the Original on a reduced scale***Fig. 1****Fig. 2**

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